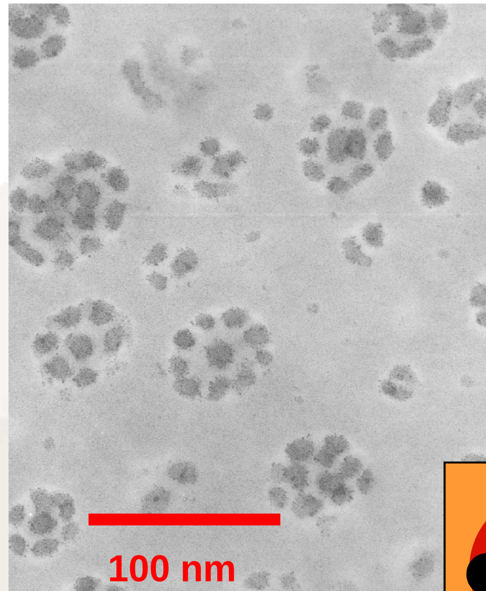
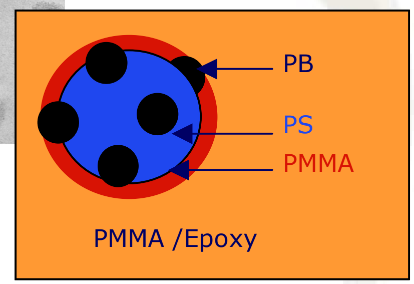
Nanostrength® Block Copolymers for Wind Energy

Robert J. Barsotti, Alexandre Alu, Grady Bentzel, Phil Allen, Noah Macy, Scott Schmidt and Michael O. Wells





NANOSTRENGTH®

Nanostrength® for Wind Energy

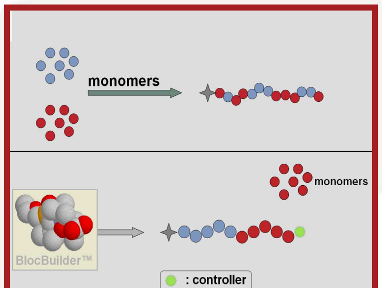
- **Arkema overview**
  - Nanotechnology platform at Arkema
- **Triblock copolymers for wind energy adhesives**
  - Nanostrength® triblock copolymers
- **Diblock copolymers for wind blade composites**
  - Toughening in epoxy and vinyl ester resins (VER) for infusion applications

Arkema Overview

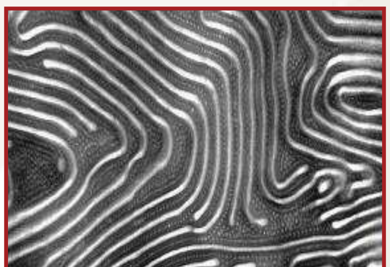
- Arkema
  - Sales: $6.0 B (2009)
  - 13,800 Employees
  - 6 R&D Centers (France, US, Japan)
  - Products include: PMMA, Fluorochemicals, Fluoropolymers, Polymer Additives, Hydrogen Peroxides, Organic Peroxides

- Arkema Inc. (North America)
  - 1,935 Employees
  - Corporate HQ: Philadelphia, PA
  - R&D: King of Prussia, PA
  - 20 Manufacturing Locations
  - www.arkema-inc.com

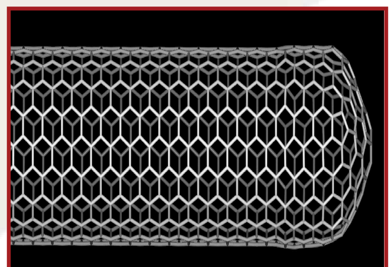
R&D – Driving Product Innovation



Controlled radical polymerization Blocbuilder®



Nanostrength® block copolymers



Graphistrength® Carbon nanotubes

Membrane for fuel cells

Nanotechnology Platform at Arkema

BlocBuilder®

CRP initiator

&

Reactivity Controller for UPR/VER

NANOSTRENGTH®

Block Copolymers

Our customers :

Compounds, Thermosets, Pigments, Engineering resins, Paints, Coatings, Adhesives,…

Functionalized Specialty Block Copolymers

&

FlexiBloc®

Reactive Block Copolymer

GraphiSTRENGTH Advanced Materials

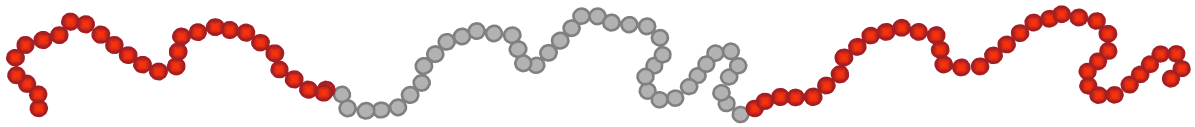
MWCNTs

Triblock copolymers for Wind Energy Adhesives

Nanostrength® Triblock Polymers

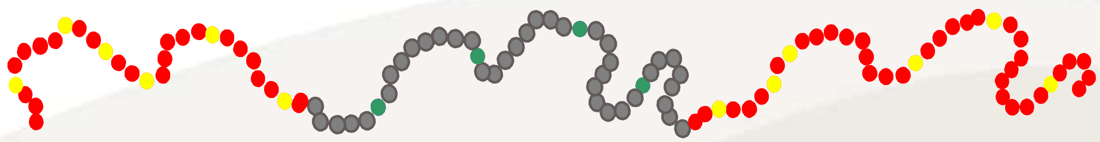
Controlled Radical Polymerization (CRP) →

MAM



Poly[(Methyl)methacrylate] -b- poly(Butyl Acrylate) -b- poly[(Methyl)methacrylate]

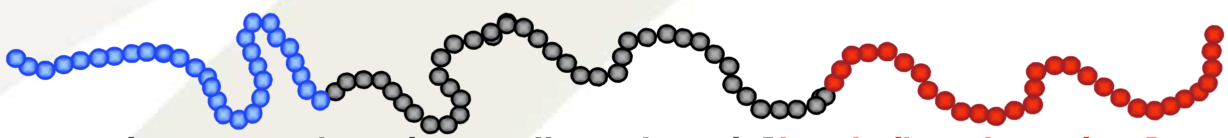
F-MAM



Functional comonomers can be added (AA, MAA, PEGMA, HEMA) to any block

Anionic polymerization →

SBM



polyStyrene -b- polyButadiene -b- poly[(Methyl)methacrylate]

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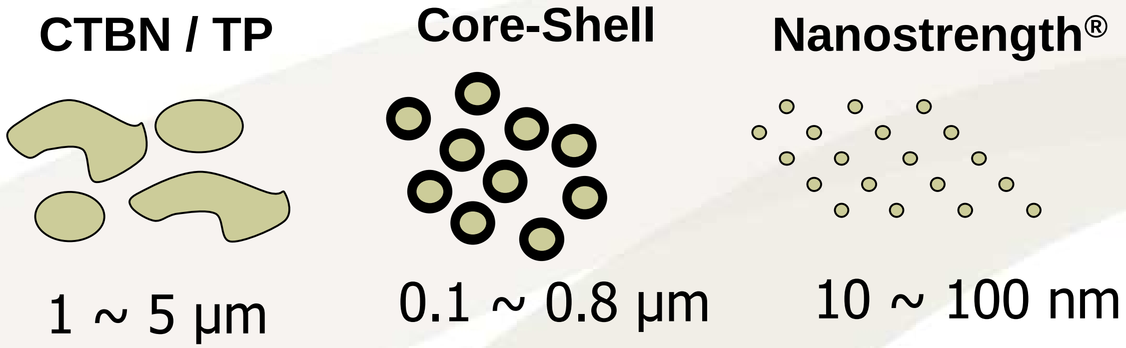
Block Copolymers for Thermoset Toughening

Nanostrength® Value Drivers

- **Balance of properties: Increased resistance to crack propagation while maintaining Tg, modulus, strength, UV and thermal properties.**
- **Novel nanostructuration: Improved toughening.**
- **Nanoscale size: Toughening of thin adhesive bond lines and composites with small inter-fiber spacing (critical for infusion)**
- **Ease of Processing: Additive dissolves in resin**



Nanostrength® Applications

- **Composites: (Wind, Construction, Industrial, Aerospace, Military, Sporting Goods)**
- **Structural Adhesives: (Wind, Transportation, Industrial, B&C)**
- **Electronic Materials (Printed Circuit Boards, Adhesives)**

Block Copolymers for Epoxy Toughening

-Affinity between epoxy monomers and PMMA
- Repulsion between epoxy monomers and the middle block(s)

→ ***Nanophase separation of PBuA blocks:***

Modifier morphology in cured epoxy dependent on:

•Crosslinking/Resin chemistry

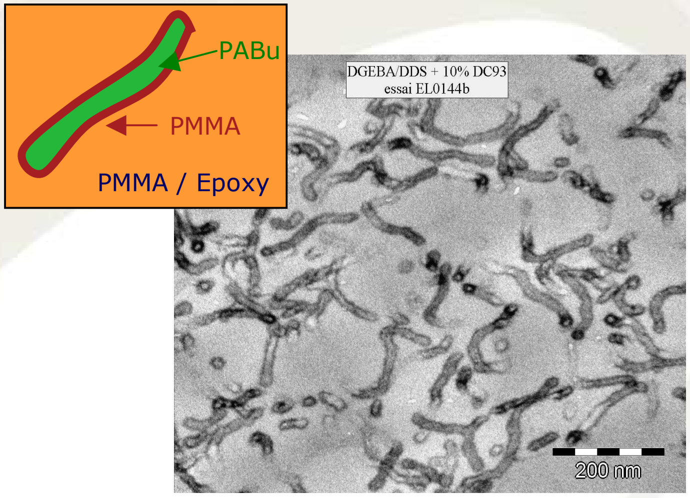
•Block Copolymer Chemistry

M52, M53: PMMA-block-PBuA-block-PMMA

Best performance with less polar curatives (polyetheramines, M-DEA)

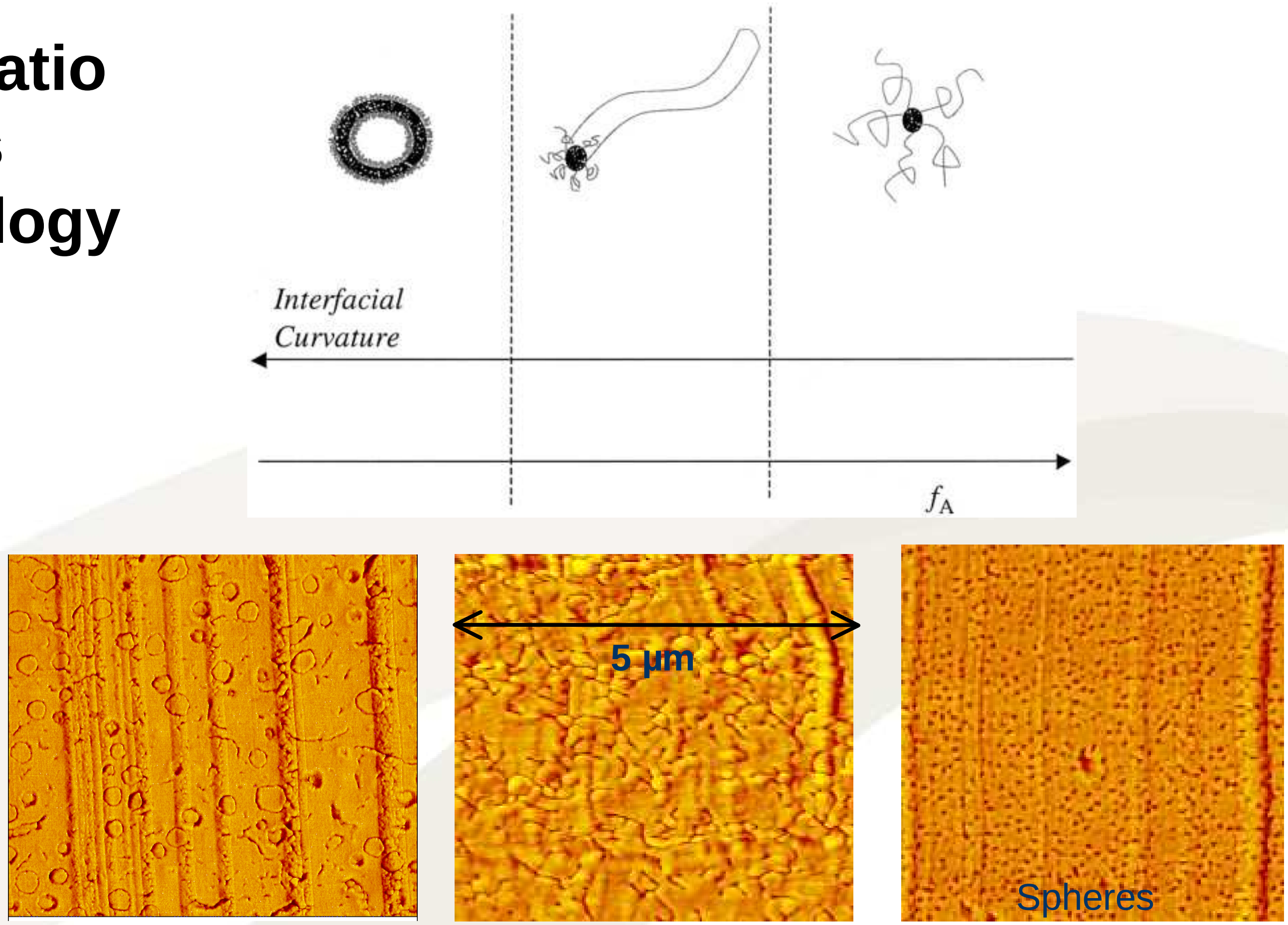
M52N: DMA functionalized MAM (Dicy, DDS)

Best performance with more polar curatives



Block Copolymers for Epoxy Toughening

Block Ratio Dictates Morphology



Vesicles

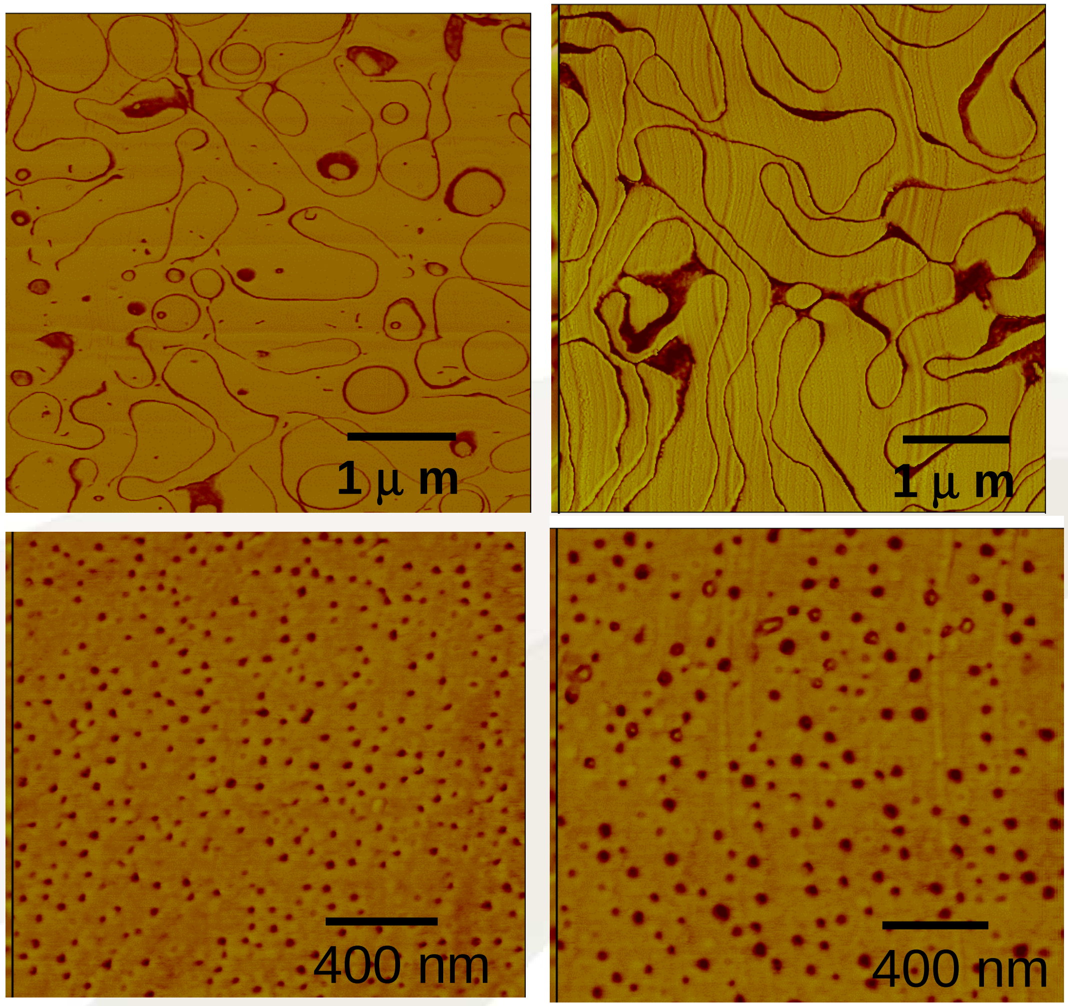
Worm-like micelles

Interfacial curvature

Dean, Grubbs, Saad, Cook, Bates J. Pol. Sci. B, 41 (2003) 2444-2456,

Block Copolymers for Epoxy Toughening

Increasing polarity of miscible block

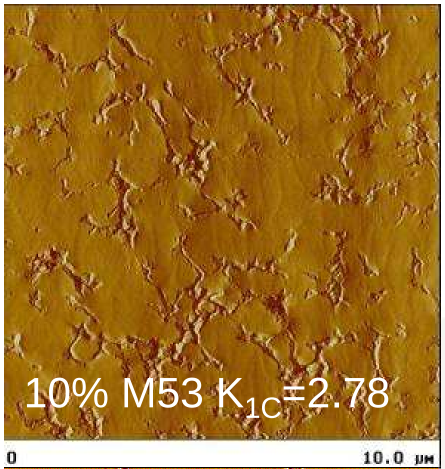


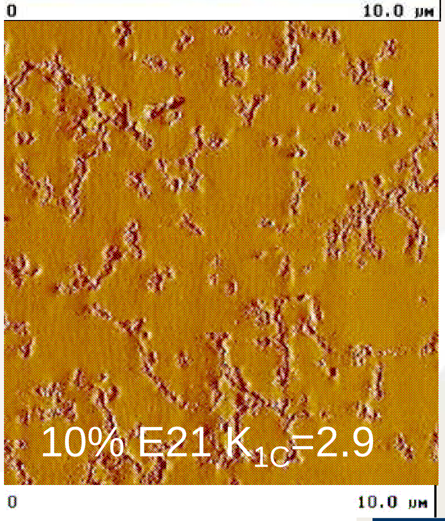
Increasing immiscible block length

Block Copolymers for Epoxy Toughening

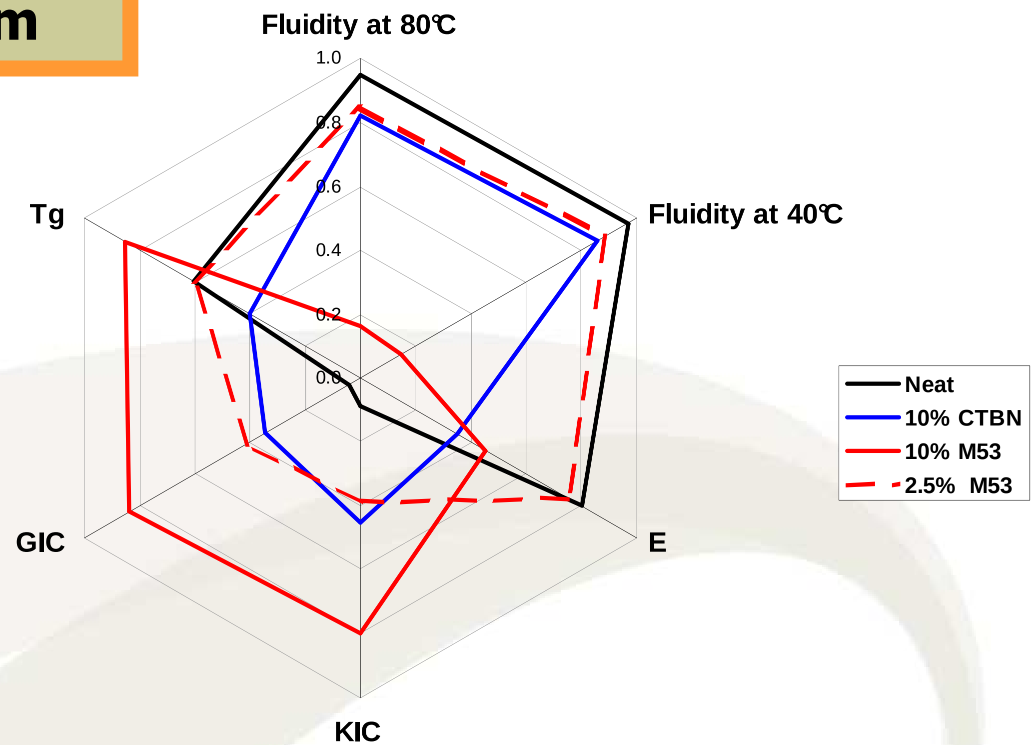
Wind Energy Adhesive System

DGEBA + Jeffamine® T403





M53 or E21 give "spider web" agglomeration for exceptional toughening



	M53			CTBN		
Loading Level	K1C	G1C	Tg	K1C	G1C	Tg
0%	0.76	183	92	0.76	183	92
2.5%	1.66	1873	92			
5%	1.71	1933	92			
7.5%	1.95	2348	93			
10.00%	2.78	3437	97	1.98	1640	85

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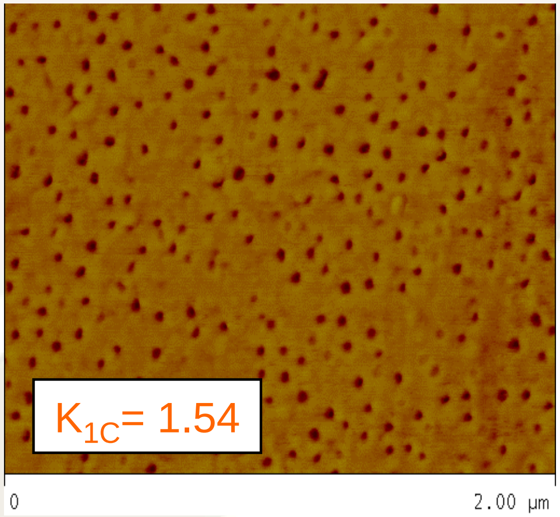
Block Copolymers for Epoxy Toughening

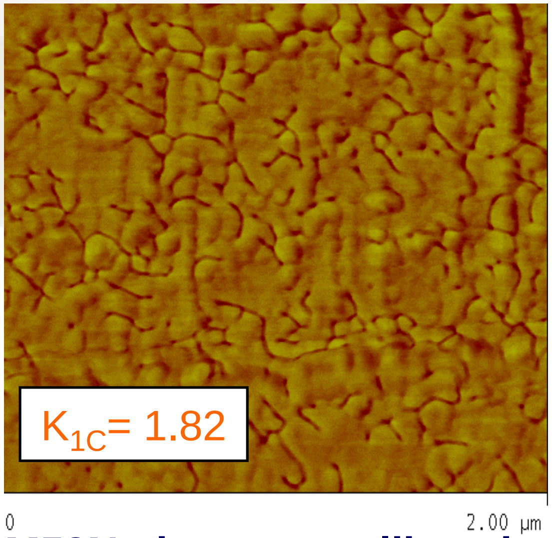
Intermediate Tg systems: DGEBA + DICY

	M52N		CTBN	
Loading Level	K1C	Tg	K1C	Tg
0%	0.88 +- 0.1	148.1	0.88 +- 0.1	148.1
2.50%	1.32 +- 0.12	146.4	1.03 +- 0.12	TBD
5.00%	1.64 +- 0.08	144.2	1.32 +- 0.12	139.1
10.00%	1.82 +- 0.11	135.4	1.62 +- 0.08	129.2

- **Excellent toughening at equivalent loadings**
- **Equivalent toughening at lower loadings**



Nanospherical micelles for transparency (exp. grade)



M52N gives worm-like micelle structure for excellent toughening

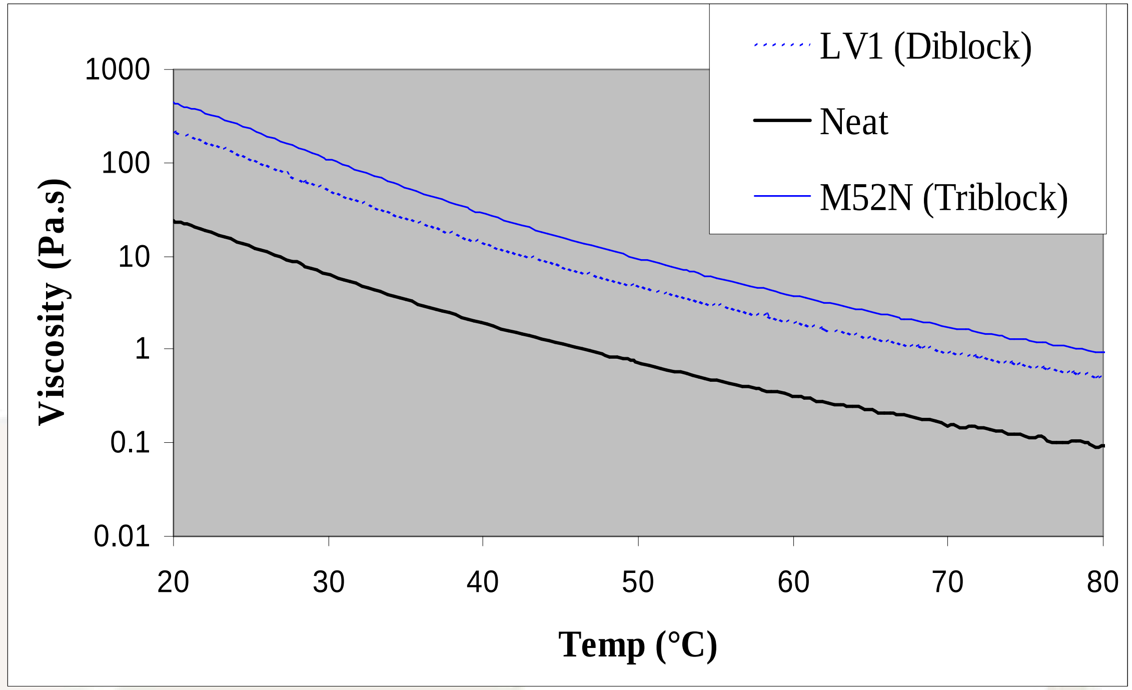
Diblock copolymers for wind blade composites

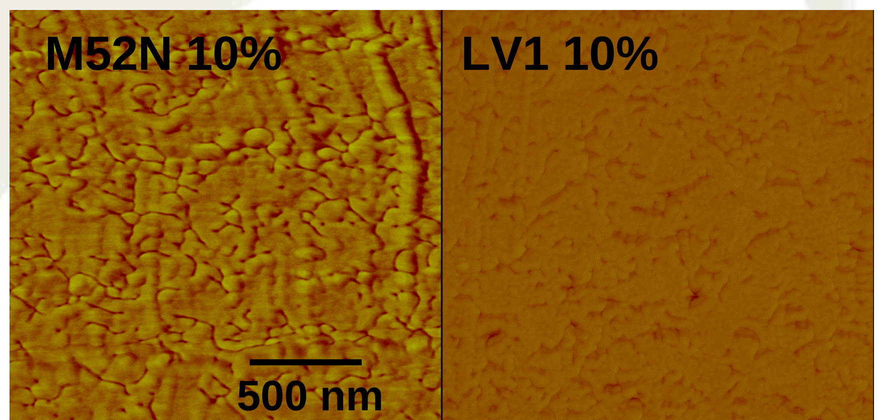
Triblocks vs Diblocks

Triblock

Diblock

Dicyandiamide cured	M52N (10%)	LV1 (10%)
K_{1C} (MPa.m$^{1/2}$)	1.82	1.86
G_{1C} (J.m^{-2})	1867	1552
Tg by DMA (°C)	135.4	128.4
Viscosity (Pa.s) at 40ºC	28.6	14.0

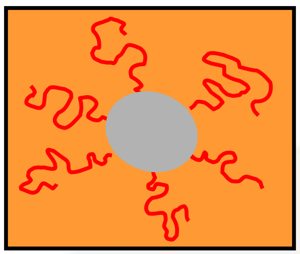


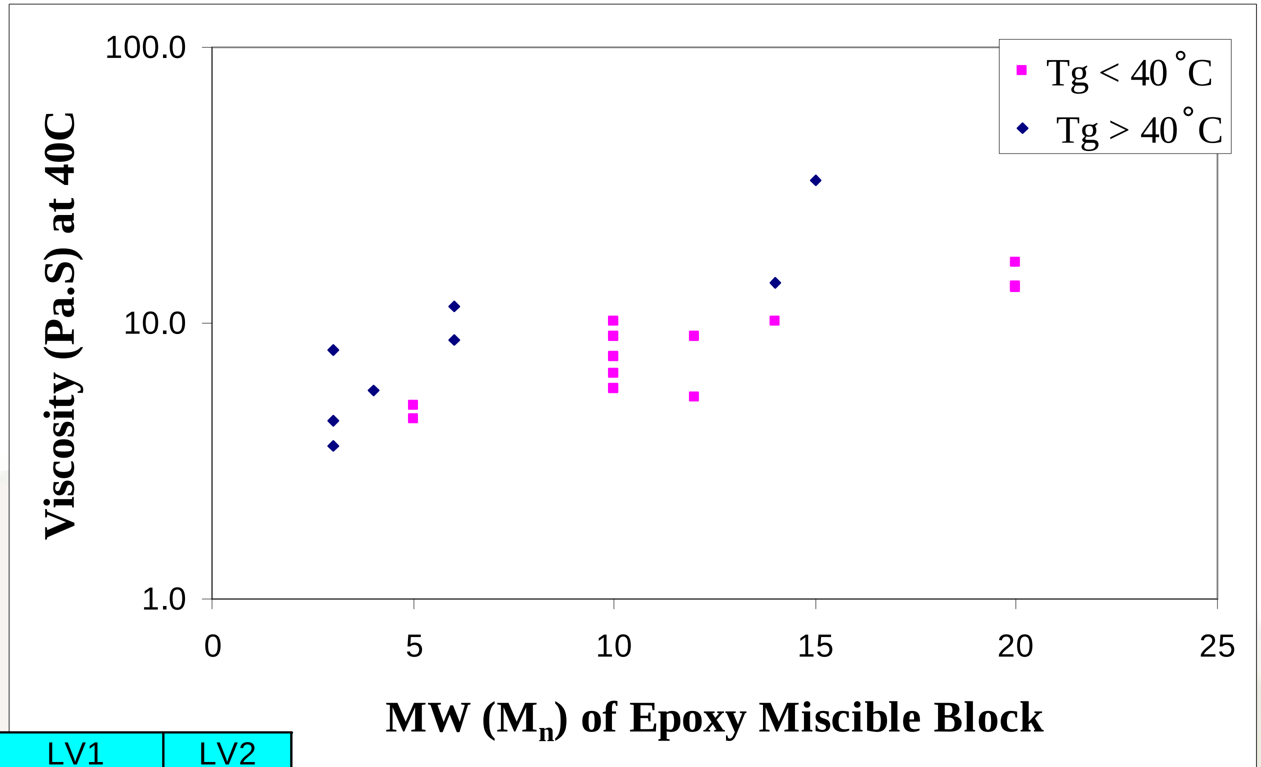


Diblock gives similar mechanical and thermal performance with ½ of the viscosity increase

Low MW, Low Tg Miscible Blocks

Use of Low MW and Low Tg miscible blocks further reduces viscosity

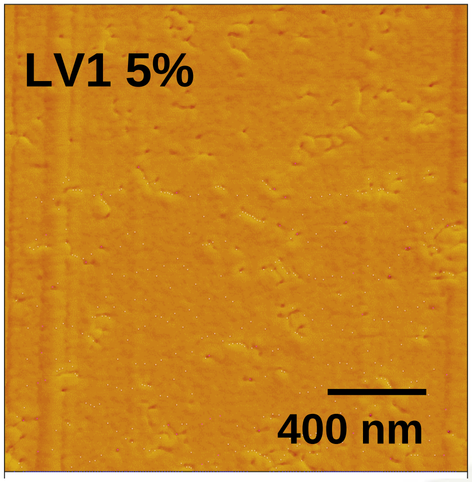


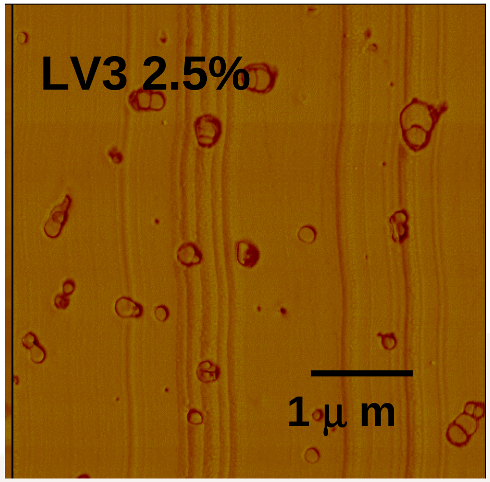


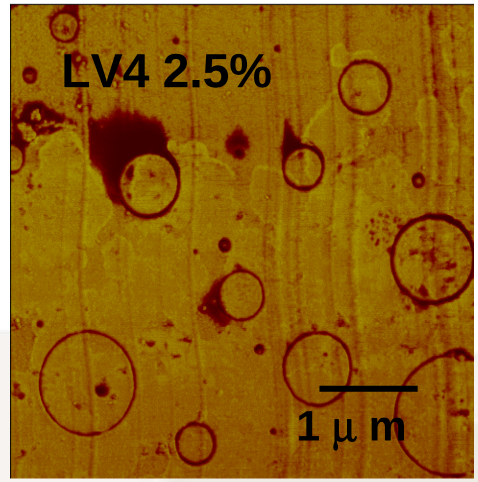
Dicyandiamide cured	M52N (10%)	LV1 (10%)	LV2 (10%)
K_{1C} (MPa.m$^{1/2}$)	1.82	1.86	1.89
G_{1C} (J.m^{-2})	1867	1552	1778
Tg by DMA (°C)	135.4	128.4	127.7
Viscosity (Pa.s) at 40ºC	28.6	14	7.45

LV2 offers comparable thermal and mechanical properties at even lower viscosity

Epoxy Infusion Systems







- Impressive increases in fracture toughness at 2.5% loading with nano-worm or vesicle structures

	NEAT	LV1 (5%)	LV1(2.5%)	LV3 (2.5%)	LV4 (2.5%)
K_{1C} (MPa.m$^{1/2}$)	0.98	2.50	2.07	2.66	2.33
G_{1C} (J.m^{-2})	481	3533	1999	4375	3258
Viscosity (Pa.s) at 25ºC	0.99	3.05	1.72	1.34	1.37
Tg by DMA (ºC)	93.4	93.1	TBD	90.8	90.4

	NEAT	LV1(2.5%)	LV3 (2.5%)
Tensile Strain @ Break	2.45%	5.19%	4.32%
Tensile Stress @ Yield (MPA)	55	75	70
Tensile Modulus (MPA)	2663	2469	2390

- Significant improvements in elongation at break and tensile stress

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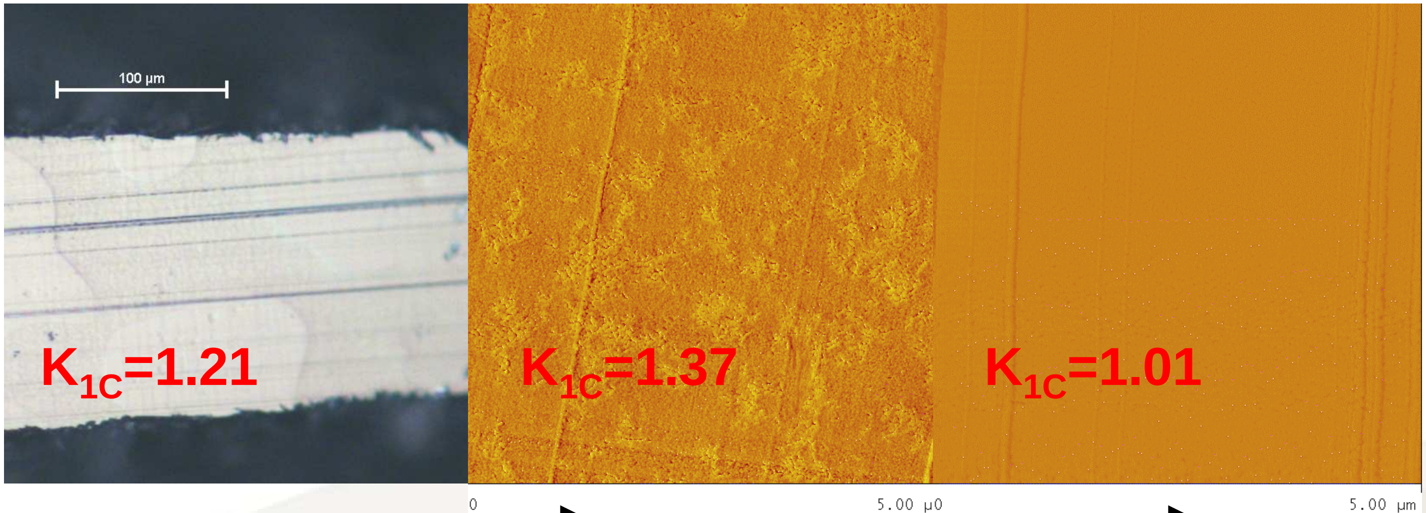
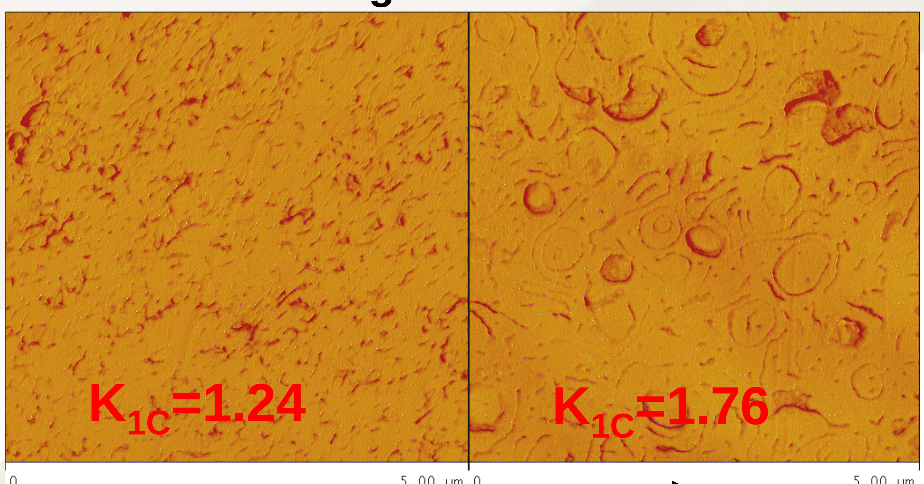
Block Copolymers for VER Toughening

High Tg miscible block



Increase miscible block length **Increase miscible block polarity**

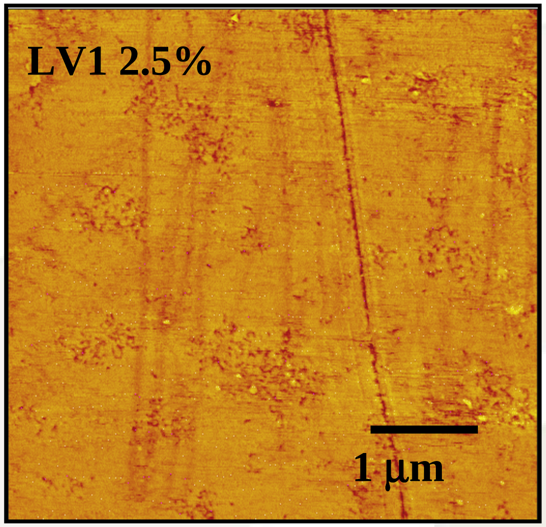
Low Tg miscible block

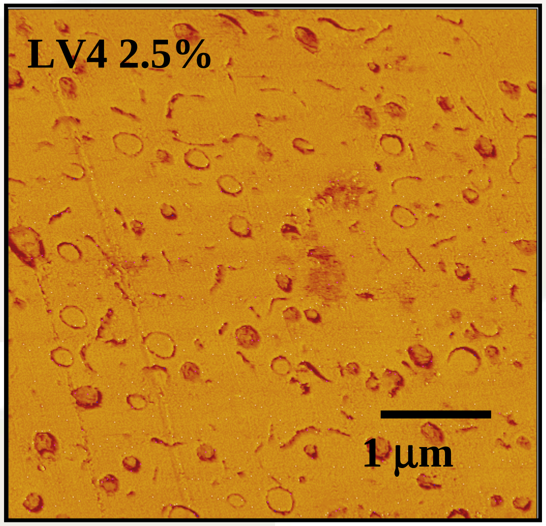


Increase immiscible block length

VER Infusion Systems

MEKP Cured	NEAT	LV1 (2.5%)	LV4 (2.5%)
K_{1C} (MPa.m$^{1/2}$)	0.51	1.04	1.17
G_{1C} (J.m^{-2})	214	629	787
Tensile Strain @ Break	0.84%	1.15%	2.21%
Tensile Stress @ Yield (MPA)	27	30	53
Tensile Modulus (MPA)	2897	2776	2741
Viscosity (Pa.s) at 25ºC	0.15	0.48	0.42





- Nanostructured rubber domains increase fracture toughness, tensile elongation at break and tensile stress at 2.5% loading
- Improvements in fracture toughness seen at very low loadings

Cook Composite
Epovia KRF1001 VE resin

MEKP Cured	NEAT	LV1 (1.25%)	LV4 (1.25%)	LV4 (0.625%)
K_{1C} (MPa.m$^{1/2}$)	0.51	0.9	1.15	1.05
G_{1C} (J.m^{-2})	214	573	801	667
Viscosity (Pa.s) at 25ºC	0.15	0.28	0.28	0.22

VER Infusion Systems

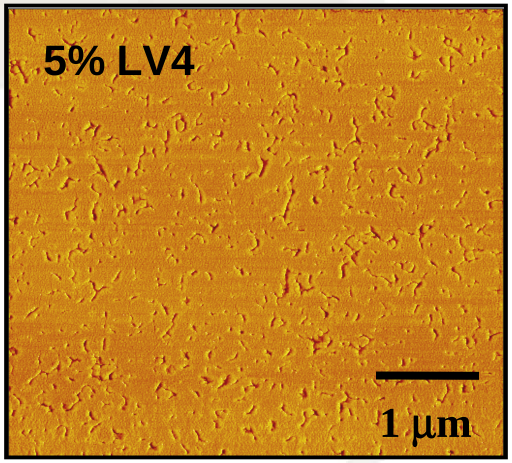
•IS300: Peroxide mixture using Arkema's BlocBuilder® technology allowing for controlled curing during infusion at elevated temperatures

	NEAT	LV1 (5%)	LV4 (5%)
K_{1C} (MPa.m$^{1/2}$)	0.72	1.89	2.17
G_{1C} (J.m^{-2})	645	2566	4382

•Excellent toughening seen in VER resin cured with IS300

•Slightly different morphology with LV4 due to elevated temperature/differing cure kinetics

•IS300 cure alleviates viscosity concerns allowing for infusion at elevated temperatures



Cook Composite
Epovia KRF1001 VE resin

NANOSTRENGTH® ARKEMA

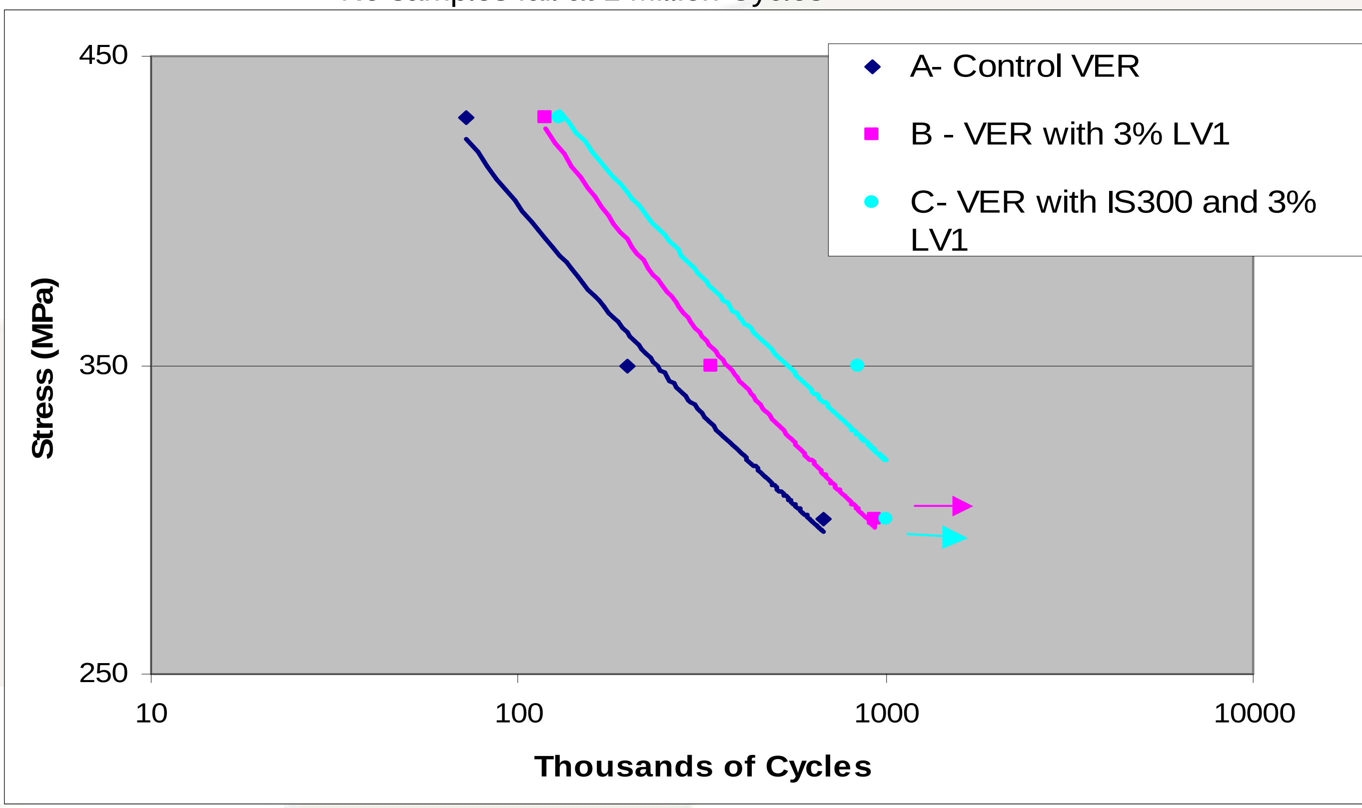
VER Infusion Systems

4 Point Bending Fatigue Testing- Infused Composite Samples

Stress Level	Thousands of Cycles		
	A- Control VER	B - VER with 3% LV1	C- VER with 3% LV1 and IS300
430 MPa	72 ± 26	119 ± 39	129 ± 50
350 MPa	199 ± 121	335 ± 88	847± 180
300 MPa	675 ± 113	938 ± 125*	>1000**

*3 out of 4 samples do not fail at 1 Million Cycles

**No samples fail at 1 Million Cycles



- Clear benefit of LV1 at 3% to increase fatigue life over unmodified VER
- Advantage more pronounced when used with IS300

Cook Composite
Epovia KRF1001 VE resin

Summary/ Path Forward

Summary

- Block copolymers allow for toughening of thermoset resins with little effect on modulus, strength or thermal properties
- The use of diblocks with low MW, low T_g miscible blocks allows for the use of block copolymers in viscosity sensitive applications
- Careful design of block copolymer architecture to achieve vesicle morphology allows for toughening at very low loading levels
- Nanostrength® block copolymers can bring value to wind energy applications by increasing the toughness of resins used for adhesives and composites

Path Forward

- Application testing in composite systems
- Structure property relationship for nanorubber for fatigue performance
- Application screening in wind blade composites and adhesives

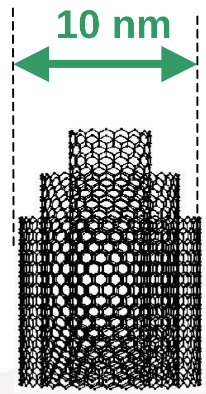
For more information, please contact: Robert Barsotti, robert.barsotti@arkema.com, 610-878-6028

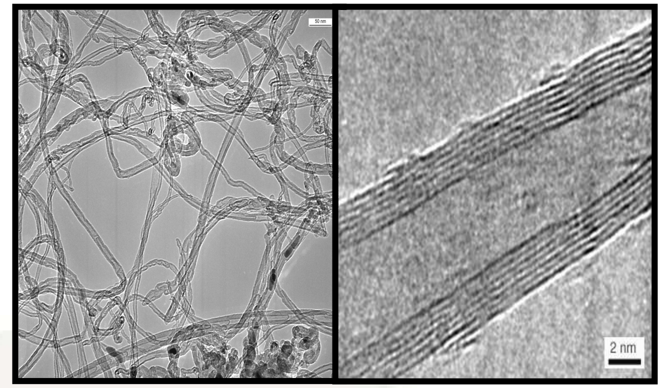
Arkema Technologies for Wind Energy

GraphiSTRENGTH®
Advanced Materials

Multi-Walled Carbon Nanotubes

Low-Weight/High-Strength





BlocBuilder®

Controlled Radical Polymerization

Reactivity Controller for Efficient Infusion of UPR and VER

Kynar Aquatec®

Aqueous PVDF Coating Technology

Increased Reliability

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